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報　文

Composition Analysis of Styrene－Butadiene Copolymer by Pyrolysis－Capillary Gas Chromatography

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A composition analysis of styrene–butadiene copolymers was studied by pyrolysis gas chromatography (PyGC) with a fused silica capillary column. The peaks of styrene, styrene dimer, strene trimer, butandiene and 4–vinylcyclohexene were detected on the pyrograms from the copolymers. The peak area of their pyrolysis products on the pyrogram were corrected by effective carbon numbers for the composition analysis. The results determined by PyGC were compared with those obtained by NMR spectrometry, and both results were good agreed. It was found that this method is applicable to simple and rapid composition analysis of styrene–butadiene copolymers.

1. INTRODUCTION

In the present HS–based Customs Tariff Schedules, the classification and the rate of customs duties of polymers differ according to whether they are homopolymer or copolymer (or polymer blend). Copolymers are defined as covers all polymers in which no single monomer contributes 95% or more by weight to the total polymer content. In the customs chemical analysis, therefore, it is necessary to determine the composition as well as confirm their kinds of polymers.

Pyrolysis gas chromatography (PyGC) provides unique information and useful data which were difficult to or impossible to obtain by other instruments such as infrared spectrometry. At customs laboratories, so far, several studies have been reported about the composition analysis of a series of styrene resins by PyGC with a packed column[1), 2)]. However, these methods are achieved using only monomeric and dimeric constituents and insufficiently separated peak with a packed column. Furthermore, these methods need a calibration curve made by measuring pyrograms of standard samples with known composition.

Recently, Kotsuji presented a simple analytical method for the composition of isoprene–styrene and styrene–pyridine block copolymers by PyGC with a capillary column[3)]. This method doesn't need a calibration curve for the composition analysis of the copolymers or polymer blends using their peak areas on the pyrogram obtained from a polymer blends with 1：1 composition contain polystyrene and polybutadiene.

The purpose of this work is to study an exact, simple and rapid composition analysis of styrene butadiene copolymers (SB) by PyGC with a capillary column based on Kotsuji's method, and the results were compared with those obtained by NMR spectrometry.

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2. EXPERIMENTAL

2.1 Substances

Standard polystyrenes (PS), polybutadienes (PB) and styrene–butadiene copolymers used in experiment are shown in Table 1. Five actual styrene–butadiene copolymers are shown in Table 2. Compositions of styrene–butadiene copolymers were determined by ^{1}H–NMR spectrometry. Composition of the copolymer of standard sample (S/B=85/15 as indication from manufacture) could not be measured by NMR spectrometry because this polymer is inoluble in many organic solvents. Accordingly, its composition is a value which was indicated by manufacturer.

Table 1 Standard samples

	Molecular weight
Polystyrene	over 20,000
	3,900
Polybutadiene	over 20,000
	5,900

Table 2 Actual samples

Sample	Styrene / Butadiene ratio
1	95.5 / 4.5
2	93.3 / 6.7
3	85.0 / 15.0
4	76.0 / 24.0
5	71.0 / 29.0
6	28.0 / 72.0

2.2 Apparatus

Measurements were carried out with a SHIMAZU GAS CHROMATOGRAPH a model GC–14A with a fused silica capillary column Ultra–1 (0.2mm i.d×25m) coated with bridged methylsilicone gum (0.33mm thick), and equipped with a curie–point pyrolyzer JAPAN ANALYTICAL INDUSTRY model JHP–3.

2.3 Measurement

About 100µg of a sample, wrapped in Pyrofoil, was inserted in quartz sample tube and pyrolyzed after temperature 150℃ for 2 minutes. The peaks on pyrogram were identified by PyGC–Mass (PyGC–MS). The measurement condition is shown in Table 3.

Table 3 Experimental conditions

GC condition	
Carrier gas :	He
Column inlet pressure :	1kg/cm^2
Injection temperature :	320℃
Detector :	FID, 320℃
Oven temperature :	50℃ → 5℃/min → 320℃
Determined pyrolysis condition	
Prolysis temperature :	650℃
Pyrolysis time :	2 sec

3. RESULTS AND DISCUSSION

3.1 Pyrogram of standard samples

Firstly, the pyrogram of standard polystyrene (Mn=50,400) was measured to make sure of whether the PyGC system is normal or not. Fig. 1 shows a pyrogram obtained from the polystyrene on the condition that the pyrolysis temperature is

500 deg. and the pyrolysis time is 4 sec. This pyrogram is very similar to that of polystyrene reported by Tsuge et al[4]. Hence it was confirmed that the system was normal and stable thermal degradation. The same result also exhibited about another standard polystyrene with different molecular weight (Mn=3,900).

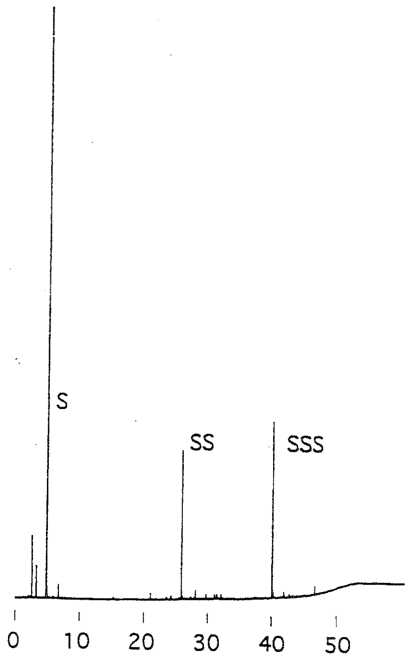


Fig. 1　Pyrogram of Polystyrene (Mn=50,400) Pyrolysis condition 500℃, 4 sec

Fig. 2 shows a pyrogram obtained from a standard polybutadiene (Mn＞20,000). Two main peaks of Butadiene (B) and 4–Vinylcyclohexene (butadiene dimer, BB) and small peaks due to groups of trimer, tetramer and pentamer were observed. A pyrogram obtained from a standard styrene–butadiene copolymer (S/B=76/24) are shown in Fig. 3. As shown in Fig. 3, some large peaks such as toluene, α–methylstyrene, etc. were also detected in addition to the main peaks of monomer (S, B), dimer (SS, BB) and trimer (SSS) which are detected on the pyrograms from each homopolymer of styrene or butadiene.

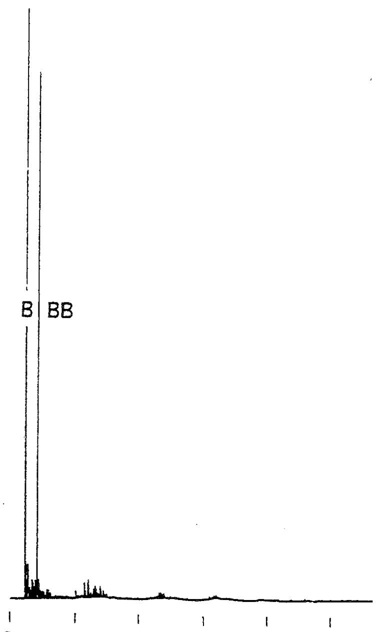


Fig. 2　Pyrogram of Polybutadiene (Mn＞20,000)
The measurement condition is same to that cited in Fig. 1

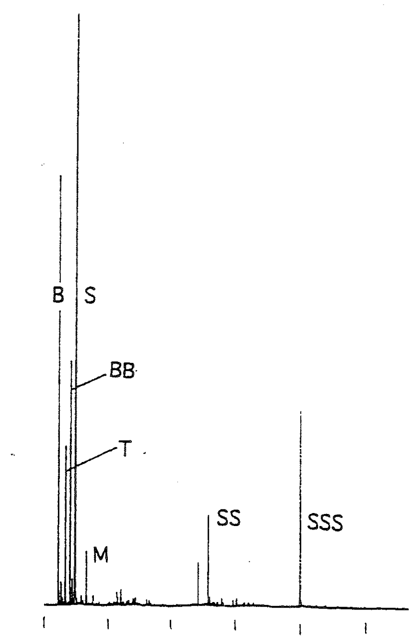


Fig. 3　Pyrogram of standard Styrene–butadiene copolymer
The measurement condition is same to that cited in Fig.1

3．2　Pyrolysis condition

Next, most appropriate pyrolysis condition was examined in view of the reproducibility (expressed as a coefficient of variation value, C.V) of $[S]_A/[B]_A$ value ($[S]_A$ and $[B]_A$ mean the peak areas of styrene and butadiene, respectively) of standard SB copolymer by changing the pyrolysis temperature of 500, 590, 650 and 740 deg., and 2 or 4 seconds of pyrolysis time. It was indicated that the C.V values results in a lowering according to rise of the pyrolysis temperature. On the other hand, the pyrogram at 740 deg. was different from those lower than the temperature, so it seemed that abnormal degradation was caused. But the C.V value was not affected by the pyrolysis time. From the above results. it was determined that pyrolysis condition is 650 deg. for 2 seconds.

3．3　Determination of Composition

3．3．1　Conventional method

First, the determination of each monomer units were performed by the ordinary method, which are used the peak areas of styrene (S) and 4－vinylcyclohexene (BB). This method needs a calibration curve to determine the copolymer compositions by plotting the peak area ratio $[S]_A/[BB]_A$ vs. the known composition. Here, we tried a simple method not using a calibration curve for the composition analysis of copolymer as follows,

for standard sample, $[S]_w/[B]_w=76/24=3.17$ ($[S]_w$ and $[B]_w$ mean the weight contents of styrene and butadiene, respectively)

the measurement value $[S]_A/[BB]_A=43.26$

The conversion factor from measured area ratio to weight ratio can be obtained by standard sample:

conversion factor (f)=43.26/3.17=13.65

So, the composition of actual sample can be calculated from equation (1) and equation (2).

$$[S]_w/[B]_w=[S]_A/([BB]_A\times13.65) \qquad (1)$$

$$\text{styrene content}=\frac{[S]_w}{[S]_w+[B]_w}\times100=\frac{[S]_w/[B]_w}{[S]_w/[B]_w+1}\times100 \qquad (2)$$

For example,

styrene; $[S]_A=99355$, $[SS]_A=3209$, $[SSS]_A=5712$

butadiene; $[B]_A=1758$, $[BB]_A=596$

$[S]_w/[B]_w=[S]_A/([BB]_A\times13.65)=12.213$

Accordingly, the styrene content

$$=\frac{[S]_w/[B]_w}{[S]_w/[B]_w+1}\times100=\frac{12.213}{12.213+1}\times100=92.4\%$$

By using equation (1) and equation (2), we determined the compositions of actual samples (Table 4).

Table 4　Comparison of styrene contents (w%) of styrene－butadiene copolymers determined by PyGC (conventional method) and by ^{1}H－NMR method

Sample	^{1}H-NMR	PyGC
1	95.5	95.6
2	93.3	92.5
3	85.0	93.0
4	76.0*	76.0
5	71.0	71.0
6	28.0	30.1

* Standard sample

Except for the sample that contain 85% of styrene component, the results were good agreement with the composition by NMR, but the reproducibility of $[S]_A/[B]_A$ value for standard sample when measurements were repeated 4 times is 6.5% as a coefficient of variation (C.V). Although this method gives accurate results but it doesn't give good reproducible results. In this study, therefore, another method was tried to determine the SB composition more precisely.

3．3．2 Correction method

Next, for the composition analysis of SB copolymer, we used their peak areas corresponding to S, SS, SSS, B and BB on the pyrogram obtained from SB copolymer. Because the sensivity of FID is proportional to the effective carbon number, peak areas must be corrected by the effective carbon number to calculate actual molar sensitivity[4), 5)]. The calculation of the effective carbon numbers are carried out by following way.

For S,

$$\underbrace{Ph}-\underbrace{C=C}$$

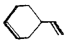
effective carbon number=1.0×6＋0.95×2＝7.9

their effective carbon numbers of SS,SSS, B and BB components are also obtained by the same way, respectively.

SS : C=C (Ph) －C－C－Ph 1.0×14＋0.95×2=15.9

SSS : C=C (Ph) －C－C (Ph) －C－C－Ph 1.0×22＋0.95×2=23.9

B : C＝C－C=C 0.95×4=3.8

BB :  1.0× 4 ＋0.95× 4 ＝7.8

Therefore the molar sensitivity for each component can be expressed as follows

$[S]_M=[S]_A/7.9+2\times[SS]_A/15.9+3\times[SSS]_A/23.9$ and

$[B]_M=[B]_A/3.8+2\times[BB]_A/7.8$ (3)

As the ratio $[S]_M/[B]_M$ is a molar ratio, it must be calculated to a weight ratio. It is not exact way to multiply $[S]_M$ or $[B]_M$ by molecular weight because the formation rate of styrene components and butadiene components differ.

Therefore, the ratio $[S]_M/[B]_M$ were corrected by the ratio of the standard copolymer.

In the case of the standard SB copolymer, $[S]_W/[B]_W=76/24=3.17$

The determined value is $[S]_M/[B]_M=5.32$

Thus, the conversion factor=5.32/3.17=1.68.

Finally, the styrene content of the copolymer of actual sample are calculated from following equations (4) and (5).

$$[S]_W/[B]_W=[S]_M/[B]_M\times\frac{1}{1.68}=\frac{[S]_A/7.9+2\times[SS]_A/15.9+3\times[SSS]_A/23.9}{([B]_A/3.8+2\times[BB]_A/7.8)\times1.68} \quad (4)$$

$$\text{The styrene content (\%)}=\frac{[S]_W}{[S]_W+[B]_W}\times100=\frac{[S]_W/[B]_W}{[S]_W/[B]_W+1}\times100 \quad (5)$$

By using equation (4) and (5), we determined the compositions of the actual samples and these determined values were compared with those obtained by ^1H－NMR (Table 5).

Table 5 Comparison of styrene contents (w%) of styrene－butadiene copolymers determined by PyGC (correction method) and by ^1H－NMR method

Sample	^{1}H-NMR	PyGC
1	95.5	96.0
2	93.3	93.0
3	85.0	76.9
4	76.0*	76.0
5	71.0	73.0
6	28.0	32.0

* Standard sample

Except for the sample 3 (S/B=85/15), the results determined by PyGC was in good agreement with the compositions by NMR. The reproducibility of [S]/[B] value for standard sample is 2.8% as a C.V. By utilizing equation (4) and (5), therefore, it is possible to determine the composition of SB precisely and accurately as well as rapidly.

Table 6　Comparison of the reproducibility of $[S]_W/[B]_W$ for standard styrene–butadiene copolymer determined by conventional method and correction method

	Conventional method	Correction method
1	44.5	5.18
2	46.6	5.19
3	40.6	5.46
4	41.3	5.43
S.D	2.81	0.151
C.V	6.50%	2.82%

The reasons of the result disagreement of the sample (S/B=85/15) with compositions by NMR is seemed as follows. This sample doesn't dissolve in organic solvents such as chloroform and tetrahydrofuran. Except for this sample, all the samples dissolve in chloroform. Pyrogram of this sample also differ from other samples. In other words, a peak on the pyrogram of this sample that is detected around 14 min which isn't observed on pyrogram from other sample. So, it is seemed that sequence–structure of this sample is different from other samples.

From the above results, we conclude that the compositions of styrene–butadiene copolymers can be determined rapidly, precisely and accurately by PyGC with a fused silica capillary column, utilizing the equation (2). More detail discussion on the relationship between the sequence–sturucture and pyrogram will be reported in near future.

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